Dispersion of Metals from Abandoned Mines and their Effects on Biota in the Methow River

Okanogan County, Washington

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Bonneville Power Administration
P.O. Box 3621
Portland, Oregon 97208

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Dispersion of Metals from Abandoned Mines and their Effects on Biota in the Methow River, Okanogan County, Washington

Dan Peplow and Robert Edmonds

Annual Report (3/15/00 through 3/14/01) (Performance Period: 3/15/00 – 3/14/03)
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College of Forest Resources
University of Washington
Seattle, WA 98195

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TABLE OF CONTENTS

1. INTRODUCTION

Abandoned and inactive mines occurring in sensitive mountain watersheds cause environmental problems in Washington State (Huchton 1998, Peplow 1998, Norman 2000). Most of the mines, developed prior to 1971, are located in the Cascade Range and northeastern Washington (Norman 2000). In Okanogan County, approximately 150 mine sites have been screened by the Okanogan Public Health Department and the Washington State Department of Ecology (Huchton 1996). Of those sites, 36 were regarded as sufficiently hazardous to warrant sampling and analysis. Twenty-five were subsequently found to contain heavy metals that exceeded criteria. Three sites, the Alder Mine, Alder Mill, and Red Shirt Mill, contain tailings, waste-rock piles, and openings that generate acid rock (ARD) and acid mine drainage (AMD).

Abandoned hardrock mines have been shown to have devastating impacts on water quality and aquatic life in impacted creeks (Norman 2000). Such an impacted system is Alder Creek in Okanogan County, Washington. In a preceeding study, results indicated that acid mine drainage and waste-rock leachate impacted the water, substrates and benthic macroinvertebrates of Alder Creek, and that the chemical and biological characteristics of Alder Creek had been altered (Peplow 1998).

In Alder Creek, the in-stream concentration of copper, cadmium, chromium and zinc exceeded Washington State's acute freshwater criteria (Peplow 2001). The benthic macroinvertebrate community responded with a reduction in both the population density and taxonomic diversity. The infiltration of subsurface acid mine drainage supersaturated with carbonates into the stream resulted in a calcite precipitation gradient that increased with distance away from the mine. It appears that the impact from the acid mine drainage and waste-rock leachate has been significant and has transformed the Alder Creek, which is a tributary of the Methow River.

At the junction of Alder Creek and the Methow River there are spawning grounds monitored by the Yakima and Colville tribes and the Chelan County P.U.D. An independent survey was conducted as part of this project by direct underwater observation (snorkeling) on September 4, 1998 to identify salmonids in Alder Creek (Peplow 1998). The species identified as present were native steelhead/rainbow (*Salmo gairdneri)* and chinook salmon (*Oncorhynchus tshawytscha).*

Two redds in the Methow River at the Red Shirt Mill were identified on 10/10/00 and 10/23/00. Two parr (presumably coho) were observed on 1/27/01 in the last pond on Alder Creek after ice melt and before water levels were sufficiently high to provide outlet.

Upper Columbia River summer steelhead, including the Methow river run, were listed under the Endangered Species Act (ESA) as “endangered” on August 18, 1997. Upper Columbia River spring chinook salmon, including the Methow River run, were listed under the ESA as “Endangered” on March 16, 1999. Bull trout in the Methow River were listed under the ESA as “threatened” on June 10, 1998. Although not an ESA listed species, summer chinook also spawn in the Methow River and have experienced a severe decline in numbers of returning adults. Summer chinook are identified as “depressed” by the Washington Department of Fish and Wildlife. While it is clear that tributaries to the Methow River have been impaired by heavy metals from abandoned mine waste, the impact of metals from historic mines on salmonid habitat in the Methow River has not been determined.

2. OBJECTIVES

The University of Washington, College of Forest Resources and the Center for Streamside Studies in Seattle, Washington, is being funded by the Bonneville Power Administration to conduct a three-year research project to measure the watershed scale response of stream habitat to abandoned mine waste, the dispersion of metals, and their effects on biota in the Methow River basin. The purpose of this project is to determine if there are processes and pathways that result in the dispersion of metals from their source at abandoned mines to biological receptors in the Methow River. The objectives of this study are the following:

1. Assess ecological risk due to metal contamination from mines near the Methow.

2. Measure impact of metals from mines on groundwater and sediments in Methow River.

3. Measure response of organisms in the Methow River to excess metals in the sediments of the Methow River.

4. Recommend restoration guidelines and biological goals that target identified pathways and processes of metal pollution affecting salmon habitat in the Methow basin.

5. Submit peer review journal publications.

When concluded, this study will contribute to the advancement of current best management practices by describing the processes responsible for the release of metals from small abandoned mine sites in an arid environment, their dispersal pathways, and their chemical and biological impacts on the Methow River. Based on these processes and pathways, specific remediation recommendations will be proposed.

3. METHODS

3.1 Site Description

The study site is located near the town ofTwisp in Okanogan County, Washington (Figure 1). The Methow River basin is located in north central Washington east of the Cascade mountains and is bordered by Canada on the north. Draining nearly 1,800 square miles, the Methow River flows southward through western Okanogan County and empties into the Columbia River near the town of Pateros. The mouth of the Methow River is located at River Mile (RM) 524 on the Columbia River in north central Washington State. The Methow watershed extends approximately 86 river miles from the confluence with the Columbia River to its headwaters located along the Cascade Crest and the Canadian border (WRIA 48).

Topography within the basin ranges from mountainous terrain along the Cascade Crest to a gently sloping, wide valley found along the middle reaches of the Methow River. Elevation ranges from 2600 m in the headwaters of the basin to approximately 240 m at the confluence of the Methow and Columbia Rivers (Habitat Limiting Factors). Topsoils in the valley consist of sandy loams that are underlain by alluvium and glacial outwash with very rapid permeability (Waitt 1972). The major groundwater aquifers of the Methow Valley exist in layers of unconsolidated sediments underlain by bedrock. Groundwater occurrence, movement and availability are primarily related to recharge sources and the configuration of depositional sediments. The Methow River and the alluvial aquifer system have a discharge/recharge relationship that varies seasonally, with specific valley position, and in relation to recharge sources (EMCON 1993).

The temporal distribution of precipitation exhibits a high degree of seasonality with roughly two-thirds of the precipitation occurring between October and March. Summers are generally hot and dry with precipitation coming from brief and intense thunderstorms. Precipitation increases in the fall and generally peaks in the winter with most precipitation in the basin occurring as snow between December and February. Since most of the precipitation occurs as snow, the seasonal distribution of runoff is strongly affected by snow storage (EMCON 1998).

Streamflow in the basin is primarily driven by runoff from melting snow. Therefore flows exhibit a strong peak during the early spring and early summer with roughly 60 percent of the mean

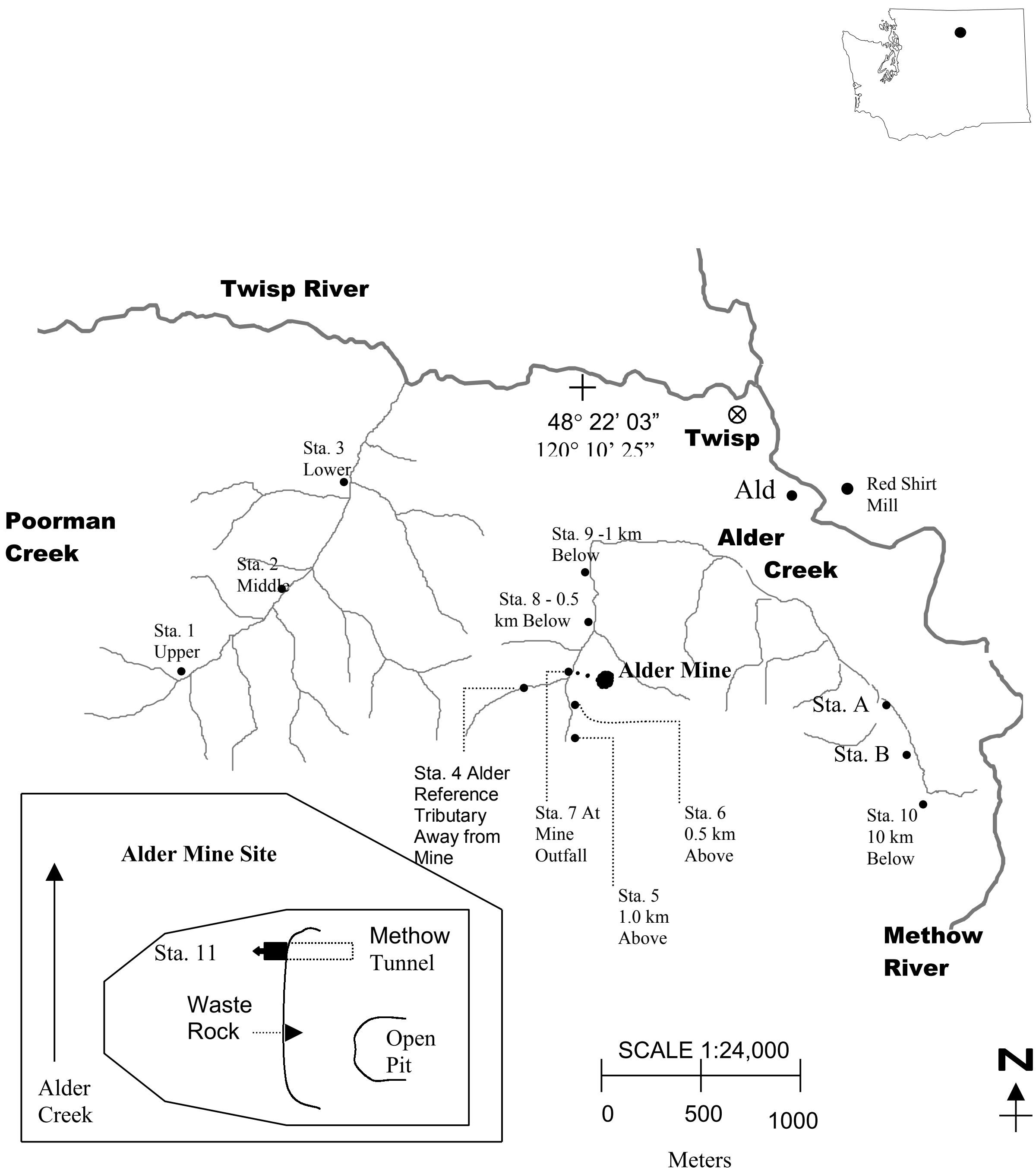

Figure 1. Map with insets showing location of Alder Creek and Poorman Creek study areas in Washington State and locations of sample stations.

annual discharge occurring during May and June (Milhous 1976, Goulder Associates 1993). Streamflow is generally high during July, then decreases from August through October in response to a reduced snowpack, low precipitation, and decreased soil moisture. Stream flow in the Methow River generally reaches an annual low during late September and early October, with some sections of streams in the basin going subsurface during dry years. Winter flows generally remain low in response to low autumn precipitation and freezing winter temperatures. Freezing temperatures retain moisture in the snopack and freeze soil moisture. Runoff between years is also highly variable as reflected in streamflow data from USGS (1996). Maximum and minimum recorded or estimated flows for the Methow River at Twisp ranged from a minimum of 134 cfs in May 1926 to a maximum of 40,800 cfs in September 1948 (Andonaegui 1995).

The role of streamflows in biologically important processes in a watershed is not reflected by mean, maximum, and minimum flows. Stream habitat depends on hydrologic processes that are measured at smaller time scales. Hydrologic conditions areinfluenced by short-term storage and release of water from snowpack and groundwater. In general, streamflows within the watershed are most influenced by snowmelt run-off and groundwater/surface water interactions. The Methow River and the alluvial aquifer system have a discharge/recharge relationship that varies seasonally, with specific valley position, and in relation to recharge sources (EMCON 19993).

Alder Mill

The Alder Mill is located approximately 1 mile south of Twisp, Washington approximately 500 m west of the Methow River at river mile (RM) 39.5. The Mill consists of several buildings and two tailings impoundments. The impoundments are estimated to contain approximately 73,000 cubic yards of material (Stewart 1995). Inputs and springs supplied by Alder Creek feed the upper impoundment creating a contaminated wetlands environment. The tailings contain significant concentrations of cyanide in addition to As, Cu, Ni, Pb, and Zn. There is eividence of groundwater contamination by As, Cd, Cr, Pb, Ni, and Se in the vicinity of the site. Private residences with groundwater wells are located adjacent to the site.

Alder Mine

The Alder Mine is an inactive mine located approximately 3 miles southwest of Twisp, Washington. The site consists of at least three partially open adits (the north adit, the south adit, and an adit in the open pit), an adit retention pond, an open pit, and waste rock dumps. The site is on the north slope of a north-trending ridge. Slopes at the site range from 50-80%. Estimates from aerial photographs inndicate that waste rock covers approximately eight acres. As, Cd, Cu, Pb, Hg, Se, Ag, and Th are present at significant concentrations in the waste rock (USEPA 2001). The discharge rate of the north adit is approximately 25 gpm and the south adit approximately 3 gpm. Be, Cd, Co, Cu, Pb, Mn, Ni, Se, and Zn are present at significant levels in the surface water.

Red Shirt Mill

The Red Shirt Mill is located approximately 1 mile southeast of Twisp, Washington approximately 500 m east of the Methow River at river mile (RM) 39.5. The mill consists of a single building and a tailings pile. The tailings pile is estimated to cover approximately 50000 square feet of surface area and contain less than 40,000 cubic yards of material. Approximately 4 m^3 of tailings are recruited annually by the Methow River and there is eividence of groundwater contamination by Pb, Ni, and Cd in the vicinity of the site. The tailings contain significant concentrations of As, Cu, Ni, Pb, and Zn. The site is located adjacent to the Twisp city limits and residences with private groundwater wells are located on and adjacent to the site.

Relatively xeric and cold forest types predominate the study area where Douglas-fir (*Pseudotsuga menziesii,* Mirb. Franco) and ponderosa pine (*Pinus ponderosa,* Dougl. Ex Lond) are the major climax species. Vegetation at the site is characterized by Douglas-fir and ponderosa pine, which dominate the overstory. Pinegrass (*Calamagrostis rubescens*) dominates the understory to the extent that other species are inconspicuous. Shrubs are normally a minor component of the stand. At the mine and mill sites, the overstory vegetation is stressed and understory vegetation is stressed or nonexistent.

3.2 Selection of Sample Stations

The location of sites for sampling tailings at the Alder Mill was determined by the locations of cores already extracted. Cores were extracted along a transect that bisects the tailings dump longitudinally. Tailings were sampled at 25 cm intervals to characterize mineralogy. Semipermenant piezometers for routine sampling of water table depth and groundwater chemistry were installed.

Two sites for monitoring the input of contaminated groundwater into the Methow River were selected based on topographical and geological indicators of a hydrological connection to the Alder Mill site. Locations for sampling sediments along the mainstem of the Methow River were selected for study based on substrate comparability. Sediments, periphyton and invertebrates were sampled at sites located at regular intervals on each side of the Methow River from below the Red Shirt Mill at approximately river mile 38 to above the Alder Mill at approximately river mile 41.

Seven deep groundwater wells located around the perimeter of the Alder Mill with casings extending to the bedrock aquifer were sampled monthly for metals and sulfate concentration head. The locations of sample stations were documented using a Trimble (Sunnyvale, CA) GeoExplorer (handheld) GPS unit.

3.3 Field Methods

3.3.1 Water.

Monthly water samples were collected in pre-cleaned teflon bottles. Subsamples were filtered (Gelman 0.45 μm, disposable 25 mm sterile disposable Acrodisc filter) for determination of dissolved metal concentrations. All water samples for metals analysis were preserved to pH<2 with 0.15% nitric acid and stored at less than 5°C. Samples for arsenic and sulfate analyses were frozen until analyzed. All analyses were performed within 30 days of sample collection.

3.3.2 Sediment

Monthly sediment samples were collected using plastic scoops at the same general locations as water samples. At each site, sediment samples were collected at a shallow depth (<5 cm) and immediately wet sieved in ambient water through a 63 μm sieve. Samples were dried to constant weight at 90°C. Sampling equipment was cleaned by washing with Liquinox detergent and sequential rinses with distilled water, dilute nitric acid, and de-ionized water.

3.3.3 Benthic Invertebrates

Specimens of the caddis fly (*Ecclisomyia sp.*) larvae were collected at regular intervals in August by hand picking larvae grazing on the surfaces of periphyton covered rocks in the Methow River. Larvae were kept in 4 oz. specimen jars containing river water and maintained live in coolers containing crushed ice until processing in the laboratory.

3.4 Laboratory Analytical Methods

3.4.1 Chemical

Samples of water, sediment, and invertebrate tissue were analyzed at the University of Washington, College of Forest Resources Analytical Laboratory in Seattle, Washington. Water samples were analyzed for total (unfiltered) and dissolved (0.45μm filtered) metals (Cd, Cr, Cu, Se, and Zn). Metal concentrations were determined by ICP atomic emission spectrophotometry (ICP-AES; Thermo Jarrell Ash ICAP 61E, EPA Method 3050). ICP-MS was used where lower detection limits were required. Samples were analyzed for arsenic by Hydride Generated Atomic Fluorescence Spectrophotometry.

A YSI model 85 meter was employed for the measurement of dissolved oxygen, TDS and temperature. Determination of dissolved-oxygen was also made in the field where flow was inadequate and YSI probe was not applicable using the Winkler Titration method (LaMotte Test Kit Model 221788). Alkalinity was measured in the field using the LaMotte Direct Read Titration Kit (Model 221780). Water temperature at each station was measured using a digital thermometer and hydrogen-ion concentration (pH) was determined using a Piccolo Model HI 1295 temperature compensated digital pH meter.

3.4.2 Mineralogical

Sediment components were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive analysis by X-rays (EDS), wave dispersive analysis by X-rays (microprobe), and infra-red (IR) spectrophotometry. The procedures used for these analyses are discussed by Carter (1993), Farmer (1974), Jackson (1969), Klute (1986), and Moore and Dennis (1989). The techniques used are not quantitative analytical procedures. However, the relative abundance of elements can be determined and their element ratios used to characterize different samples using these methods.

A bulk sample of sediment from the Methow River below the Red Shirt Mill was treated with hydrogen peroxide to remove organic matter. Subsamples were also treated with citrate buffer and sodium dithionite to remove iron oxides. Both samples were sieved (63µm) to remove the sand fraction. Particle size separation by sedimentation were employed to remove the clay fraction. Oriented clay mounts from samples with organic matter and oxides removed were analyzed by XRD. Clay mounts of samples with only the organic matter removed were analyzed by IR. Samples of silt with only the organic matter removed were analyzed by SEM, EDS and microprobe.

XRD analyses was performed using a Scintag model XGEN-4000 with Scintag software (DMSNT, version 1996) that includes the ICPD international database. A Jeol TSM-330-A scanning electron microscope that includes SQ/SSQ software was used for scanning electron imaging (SEI) and EDS. Microprobe analysis was performed on a Jeol model 733 with Geller Automation EDS software. IR analysis was performed using a Perkin Elmer 1600 Series FTIR model spectrophotometer.

3.4.3 Histopathological

Cross-sections 4 mm from the anterior end of the midgut from caddisflies were mounted for examination by transmission electron microscopy and analyzed for the accumulation of intramitochondrial granules of divalent cations according to conventional histological techniques in the Zoology laboratory at the University of Washington.

3.5 Quality Assurance/Quality Control

Selection of study sites and sample stations depended on the goals and objectives of the study. Access, location of contaminant sources, mixing zones, and dilution of pollutants were considered. Reference sites were selected that were as similar as possible to the study site. After obtaining measurements for in situ parameters, samples were collected for water-quality analyses in the order of the parameters' decreasing sensitivity. Deionized water was exposed to the sampling equipment and added to sample containers containing preservative. Field blanks and spikes were prepared in the field under the same conditions as field samples. Samples of water with known amounts of metals were submitted with test samples.

4. INITIAL ASSESSMENT OF IMPACT BY INORGANIC CONTAMINANTS FROM MINES NEAR THE METHOW RIVER

4.1 Introduction

The first phase of this project includes an analysis to determine the ecological risk of exposure to toxic chemicals from abandoned mines bordering the Methow River (RM 39.5) near Twisp, WA. For inorganic contaminants, an analysis of exposure usually involves consideration of sources, transport, partitioning of the chemical among various environmental media, chemical and biological transformation (speciation), and the identification of potential routes of exposure. In this study, the accumulation of metals (e.g., Cu) and metaloids (e.g., As) at levels over reference area background levels is used as chemical evidence of contamination. The results will be used to identify general environmental problems, establish priorities, and provide a basis for future research to characterize the ecological effects of inorganic contaminants on salmonid habitat in the Methow River.

4.2 Materials and Methods

Plants. Samples of needles from four Douglas-fir (*Pseudotsuga menziesii,* Mirb. Franco) and four aspen (*Populus tremuloides*) were analyzed for metals by ICP-AES. Metal concentrations were compared to results for reference samples from trees that were not in contact with abandoned mine waste or its effluents.

To determine whether cultivated grain crops concentrate metals from AMD contaminated streamwater, triplicate samples of oat seeds, leaves and stems were collected from a field irrigated with water contaminated with AMD. Subsamples were analyzed for metals by ICP-MS. Metal concentrations were compared to results for samples from a reference field irrigated with metal-free water.

Invertebrates. Aspen leaf miner larvae from aspen leaves were collected for metals analysis by ICP-MS. Whole-body metal concentrations were compared to results from samples of leaf miner larva from leaves growing on sites not contaminated by abandoned mine waste or effected by its effluents.

Bears. The exposure of resident bear to As was determined using the bear hair capture technique. A USGS recipe was used to prepare a non-consummable liquid lure. Scent attractant was placed on a log enclosed by a strand of barbed wire stretched approximately 50-cm above the ground to snag hair. The use of this scent to attract bears to the hair ensured there was no possibility of food reward. Three samples of hair from stations in the vicinity of the Alder Mine were collected for analysis. Arsenic concentrations in hair were compared to concentrations in reference samples from bears in captivity fed controlled diets and in environments free of As.

Cows Milk. Milk was collected from five lactating milk cows grazing in the Alder Creek watershed in the vicinity of the mine. Samples were analyzed for metals by ICP-AES. Metal concentrations were compared to results for reference milk samples from cows grazing in the Poorman Creek watershed.

Trout. Resident trout from a farm pond fed by water from Alder Creek, which is contaminated by metals from the abandoned Alder Mine, were assayed by ICP-AES for metals in their gills, liver, heart and muscle tissues. Results were compared to metal concentrations in tissue samples from fish in the Twisp River that had not been contaminated by mine waste.

Groundwater. Six domestic drinking water wells around Alder Mill, on Alder Creek below Alder Mine, and adjacent to Red Shirt Mill and two reference wells isolated from mine impacts were sampled once monthly from the well casing using disposable Teflon bailers. Samples were analyzed for metals by ICP-AES. Samples were also analyzed for arsenic by Hydride Generated Atomic Fluorescence Spectrophotometry.

4.3 Results and Discussion

Plants – Douglas fir and Aspen

Zn, Cd, Se, Mn, and Cu were elevated in Douglas fir and Aspen leaves growing on soil contaminated by waste rock from Alder Mine. Sulfur was also elevated. The results for Cu in the contaminated plants, which were > 1.5 times the reference plant concentrations, are presented in Figure 2. At 5 mg kg^{-1} (Douglas fir) and 18 mg kg^{-1} (Aspen), the results are within the normal range for Cu in plants, which is 5-20 mg kg^{-1} (Allaway 1995). Because toxicity varies with plant species and ambient conditions, a single value for Cu concentration associated with toxcity cannot be defined. Cu is an essential element for plants. Cu in plants has a role in normal enzyme activity and excessive concentrations have been associated with changes in cell membrane permeability (Allaway 1995).

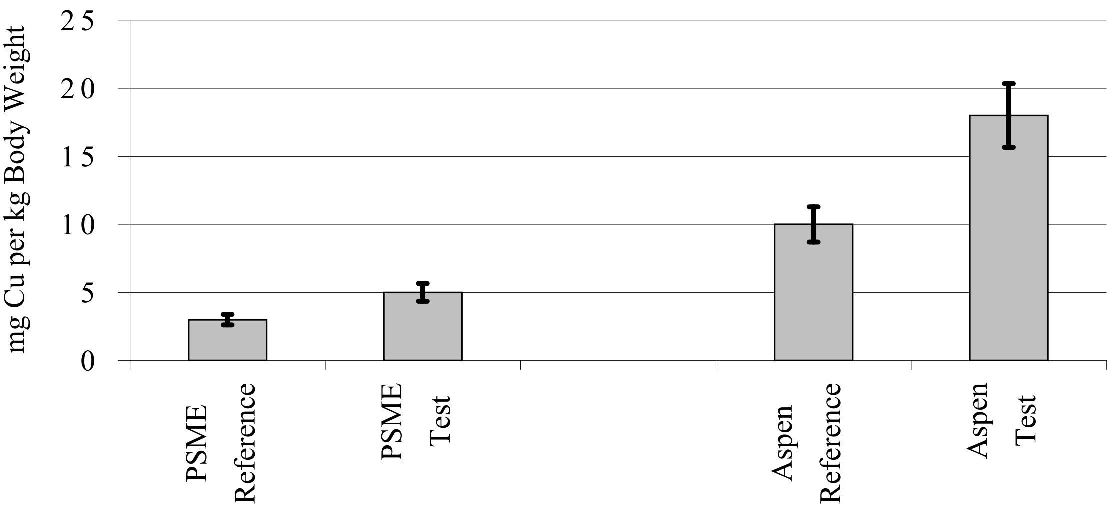

Figure 2. Concentration of Cu in Douglas fir (PSME) and Aspen growing on site contaminated by mine waste compared to plants growing on uncontaminated referrence site.

Oats

Zn, Cr, Cd, and Cu were elevated in oat seeds just prior to harvest. The oats had been grown in a field irrigated with water from Alder Creek 1 km below mine outfall. Metal concentrations ranged, in order, from 1.4 to 1.8 times the concentrations found in oats from a reference field irrigated with Methow River water that did not contain measurable amounts of metals. The metals that are the most toxic to higher plants when present in excessive amounts are Hg, Cu, Ni, Pb, Co, and Cd. Cu concentrations were 1.8 times the reference concentrations (Figure 3). Food plants that tolerate elevated concentrations of metals are likely to create a greater health risk than those that are sensitive and show symptoms of toxicity.

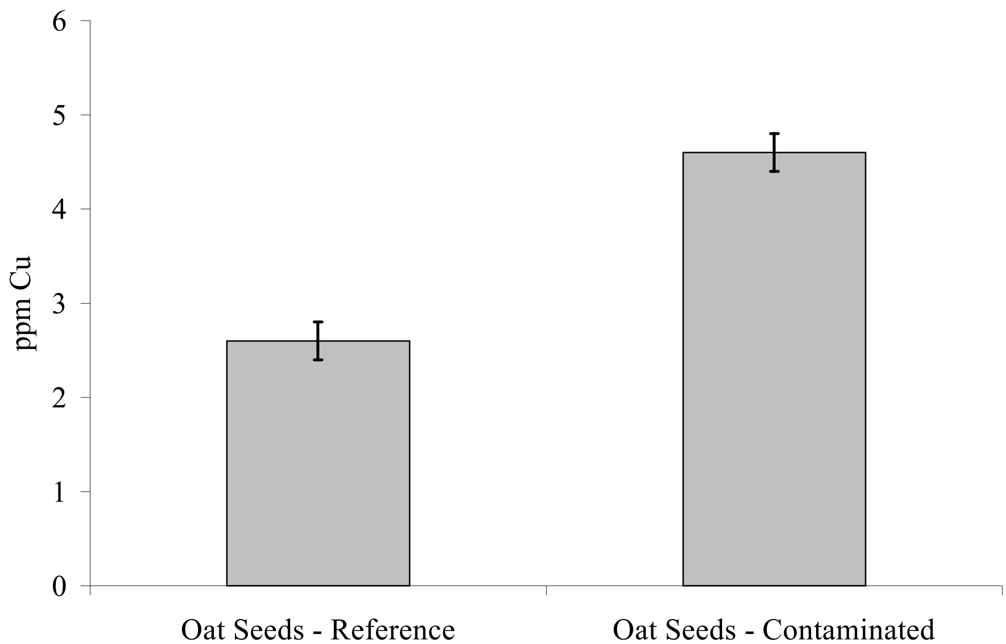

Figure 3. Concentration of Cu in oat seeds from field irrigated with metal contaminated creek water compared to seeds from reference field irrigated with metal-free river water.

Invertebrates

Zn, As, Cu, Pb, and Cd, in Aspen Leaf Miner larvae from aspen leaves from trees growing on soil contaminated by waste rock from Alder Mine ranged in order from 4 to 17 times their concentrations in larvae from the uncontaminated reference site. The results for Cu in larvae feeding on leaves with excess Cu, which was 10 times the reference larvae concentration, are presented in Figure 4. Since it is assumed that the amount (µg Cu per kg body weight) is quantitatively linked to the amount of metals originally contacted by the organism, the disproportionate magnification of Cu in larvae in contaminated leaves suggests that this element may be concentrated in the parechyma of the leaves upon which the larvae feed and that the concentration of Cu in Aspen leaves may be greater than the 1.5 fold increase reported above.

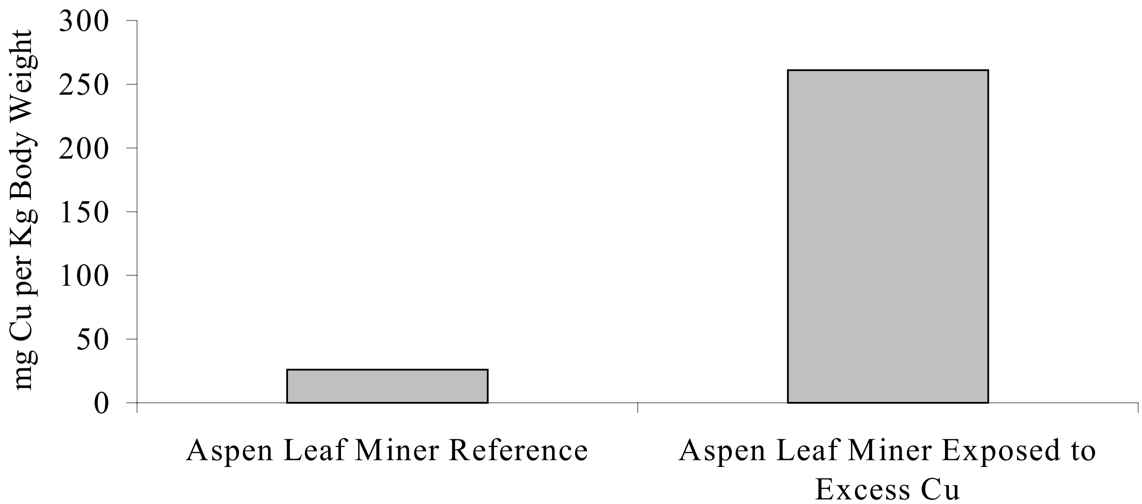

Figure 4. Concentration of Cu in Aspen Leaf Miner larvae exposed to excess Cu in aspen leaves growing on a site contaminated by mine waste compared to larvae in leaves growing on uncontaminated referrence site.

Bears

Arsenic was found to accumulate in the hair of 3 bears in the vicinity of the Alder Mine (Figure 5). Arsenic tends to accumulate in hair and is considered a useful indicator of exposure to arsenic over the past 6-12 months (USDHHS 2000). The normal level of As in human hair is < 1ppm. It should be noted that the pattern of As metabolism in bears is unknown and may not be similar to humans. The average concentration in the exposed bears was 0.77 ppm, or 17 times the average for As in the hair of the 2 reference bears (0.045 ppm) that were maintained in captivity. One individual from the contaminated site had As in their hair at 1.14 ppm. When elevated levels of arsenic are detected, it shows that there has been exposure, but unless more is known about when exposure occurred, and for how long, it is not possible to predict whether there has been any harmful effects. Ingestion of arsenic in dirt may be an important route of exposure for bears.

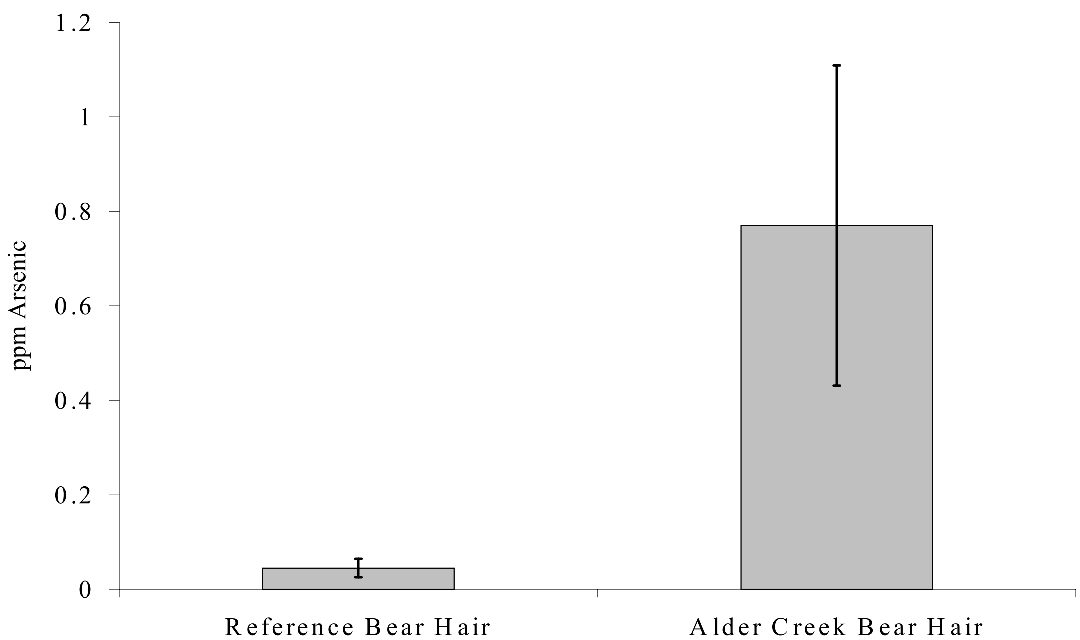

Figure 5. Arsenic concentration in bear hair from Alder Creek compared to reference bear hair.

Cows Milk.

Zn, As, Pb, Ni, and Se in milk from lactating cows grazing in the area around the Alder Mine site ranged, in order, from 1.5 to 34 times the aquatic use criteria (As, Se and Zn) and drinking water criteria (Pb and Ni). As was 3 times higher than the aquatic use criteria (Figure 6). No metals were detected in the milk of cows in the reference area.

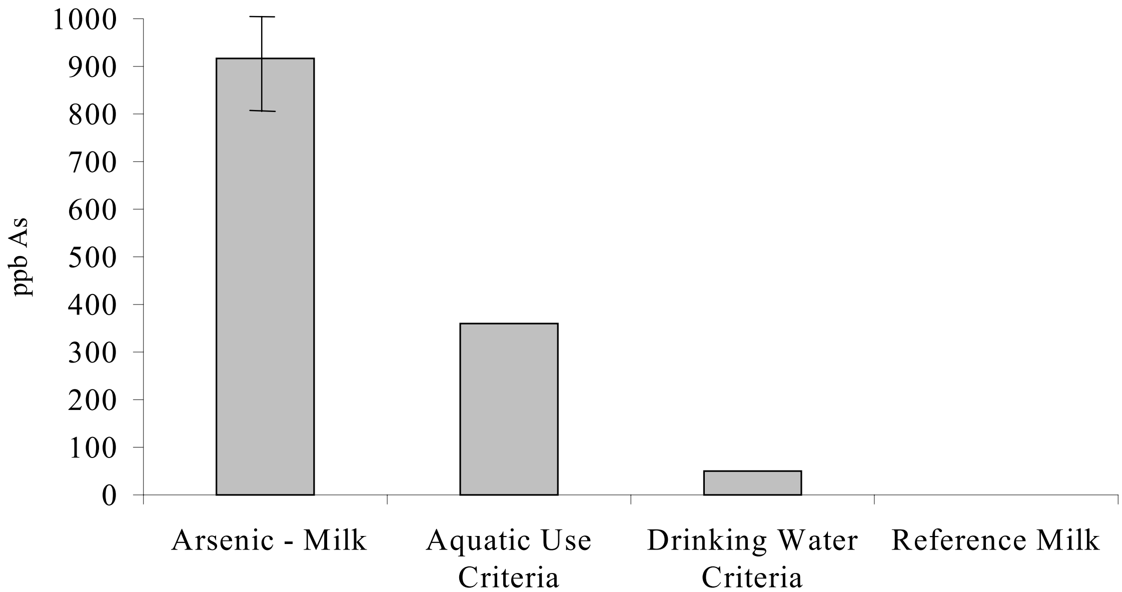

Figure 6. Concentration of As in milk of cattle grazed on mine site compared to surface and drinking water criteria and milk from cattle grazing in watershed not contaminated by mine waste.

Trout

Cd and Zn were elevated in the gills of trout exposed to excess metals in water from Alder Creek. Cd was elevated in the liver compared to tissue samples from trout in the uncontaminated reference stream (Figure 7). Cadmium is a relatively rare metal that has no essential biological function and is highly toxic to plants and animals (Alloway 1995). The major hazard to human health from Cd is its chronic accumulation in the kidneys where it can cause dysfunction if the concentration exceeds 200 ppm. Future histopathological studies should include kidney samples.

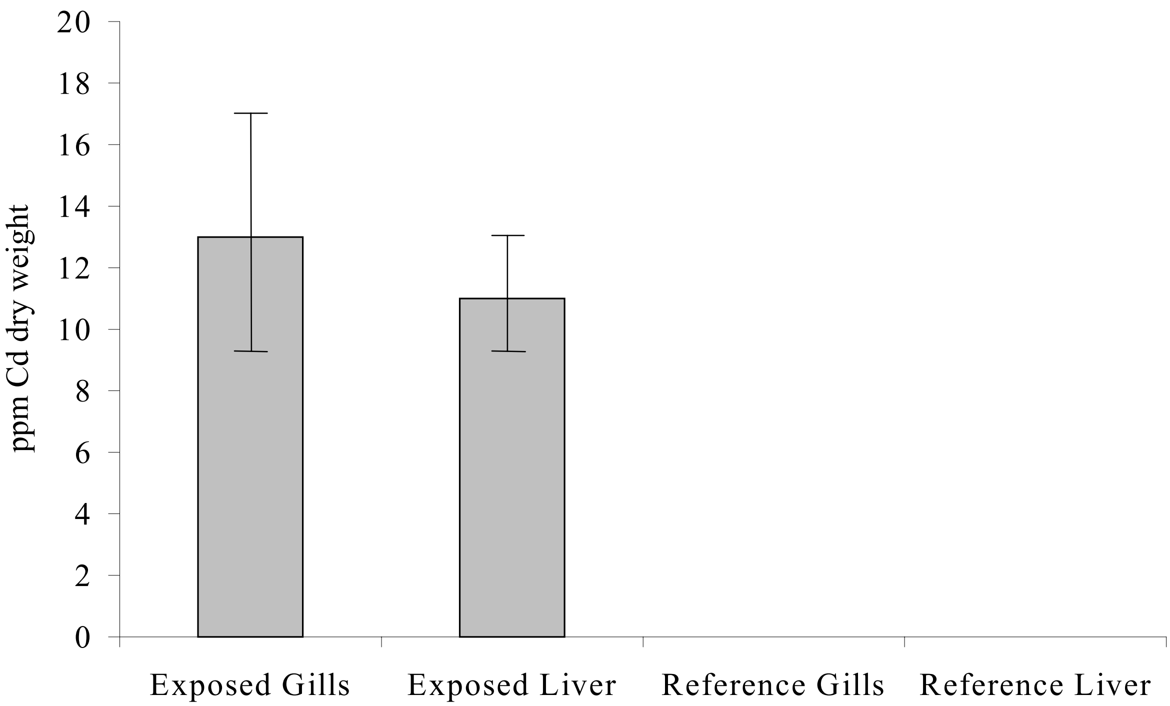

Figure 7. Cd accumulation in liver and gills of exposed trout compared to unexposed trout in reference stream.

Groundwater

Five elements (As, Cd, Pb, Ni, and Se) exceeded background levels as well as drinking water criteria in water from domestic wells. A trend is apparent and elevated metal concentrations (Cd, Pb, Ni, and Se) appear to coincide with spring runoff. The trend in As concentrations is given in Figure 8. Since it is generally assumed that essentially all ground water contained in the alluvial/glacial aquifers in the Methow basin, including the tributary valleys, is in hydrolic continuity with the surface water, the occurrence of As in groundwater adjacent to the Methow River poses a threat to salmonid habitat.

Arsenic is one of the most toxic elements to fish (Irwin 1997). Acute exposure can result in immediate death due to As-induced increases in mucus production, which causes suffocation or due to direct detrimental effects on the gill epithelium. Chronic exposures can also result in the accumulation of As to toxic levels. The detoxification role of the liver may lead to abnormal cell proliferation and tumors (neoplasia) in the liver.

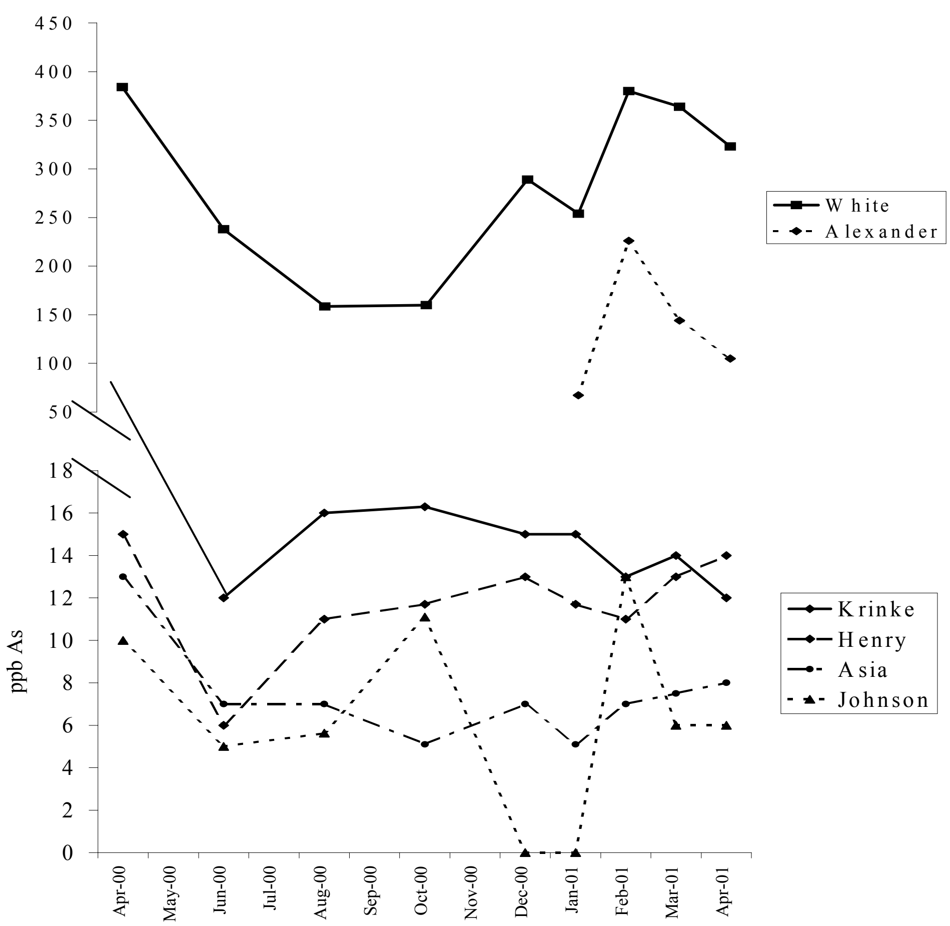

Figure 8. Trend in groundwater As concentration in six domestic wells between April 2000 and April 2001.

Conclusion

The results of this initial assessment of impacts by metals from abandoned mines in the vicinity of the Methow River indicate that there is a potential for environmental problems due to contamination by Cu, Cd, As, Pb and Zn, which were found to be the most common contaminants in Douglas fir needles, aspen leaves, phytophagous leaf miner larvae, bears, milk from lactating mammals, trout, and in groundwater. Ni, Se, Cr, Mn and S were also detected, at concentrations that exceeded background levels, in some samples exposed to contaminants from abandoned mine sites. Future research to characterize the ecological effects of inorganic contaminants on salmonid habitat in the Methow River should consider sources, transport, partitioning of the chemical among environmental media, chemical and biological transformation (speciation), identification of potential routes of exposure and the biological significance of exposure of organisms in the Methow River to elevated levels of As and Cd or Cu.

5. SOURCES AND TRANSPORT OF INORGANIC CONTAMINANTS FROM ABANDONED MINES IN THE VICINITY OF THE METHOW RIVER NEAR TWISP, WA

5.1 Inroduction

Research to characterize the ecological effects of inorganic contaminants from abandoned mines on salmonid habitat in the Methow River should consider sources, transport, partitioning of the chemical among environmental media, chemical and biological transformation (speciation), and identification of potential routes of exposure. The biological significance of exposure of organisms in the Methow River to elevated levels of As and Cd or Cu will be covered in Section 6.

5.2 Materials and Methods

Ore and tailings samples were studied using wave dispersive analysis by X-rays (microprobe) and ICP atomic emission. River sediment samples were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive analysis by X-rays (EDS), wave dispersive analysis by X-rays (microprobe), and infra-red (IR) and ICP atomic emission spectrophotometry. River sediment samples were studied using X-ray diffraction (XRD). Metal content of soils was determined by ICP atomic emission spectrophotometry. Samples assayed for arsenic were analyzed by Hydride Generated Atomic Fluorescence spectrophotometry.

The walls of four bore holes in the tailings impoundment were sampled at 25 cm intervals and analyzed for metals by ICP atomic emission spectrophotometry. Wells were installed and groundwater sampled monthly for metals. Groundwater was filtered (Gellman 0.45 µm, HT Tuffryn Membrane, disposable 25 mm sterile disposable Acrodisc filter) to measure the dissolved metal concentration.

Sediment samples from the Methow River 100 m below the Red Shirt Mill were treated with hydrogen peroxide to remove organic matter. Subsamples were also treated with citrate buffer and sodium dithionite to remove iron oxides. Samples were also sieved (63µm) to remove the sand fraction. Particle size separation by sedimentation was employed to remove the clay fraction. Oriented clay mounts from samples with organic matter and oxides removed were analyzed by XRD. Clay mounts of samples with only the organic matter removed were analyzed by IR. Samples of silt with only the organic matter removed were analyzed by SEM, EDS and microprobe.

Sodium chloride (NaCl) injections at Alder Mine were used to calculate solute budgets in the AMD between its source and input to Alder Creek and estimate the subsurface dispersion rate. It was assumed that chloride behaved conservatively. Solute was injected into the AMD discharge stream at station 13. AMD flow was diverted to a 227 L plastic reservoir containing 68 kg NaCl, which was dissolved to a final concentration of 300 g/L (180 g Cl/L). Samples were taken from a well (station 14) 50-m downslope and from the end of the subsurface AMD flow path 3-m prior to its confluence with Alder Creek. Water for chloride analysis were stored on ice in the field, and then refrigerated in the lab for less than four weeks until analyzed by ion chromatography (IC). Conservative solute transport was monitored using chloride analysis of water samples by IC analysis and in situ electrical conductivity readings.

Sulfate profiles were used to evaluate hydraulic continuity between acid mine drainage at Alder Mine, acid rock drainage at Alder Mill, Alder Creek surface water, groundwater, and the Methow River. It was assumed that sulfate was conservative and that the redox conditions favored sulfate over sulfide.

Periphyton samples in the Methow River were analyzed by ICP-MS for metal content and Hydride Generated Atomic Fluorescence spectrophotometry for As.

5.3 Results and Discussion

Source

The major component of a tailings sample taken 200 cm below the surface, based on the results from wave dispersive analysis by X-rays (microprobe), showed that plagioclase feldspars were the most common at 26% (Table 1). Minor components were quartz at 14%; chlorite at 12%; and hornblende, magnetite/hematite, muscovite, zircone, and chlinopyroxine at 5-6%. Trace elements include apatite, epidote, ilmenite. The elevated levels of Cu, Cd, and As suggests that these elements may be present in trace amounts below the limits of detection by microprobe analysis (Table 2). The concentration of Cu, Cd in tailings and waste rock at the Red Shirt Mill, Alder Mill and Alder Mine range from 7 to 171 times their estimated natural background values (Table 2). Arsenic was not assayed in either the tailings samples or waste rock, but it was assayed in forest soil below the Alder Mine and was detected at levels over three times the natural background level.

Table 1. Mineralogy of tailings sample at 200 cm by microprobe analysis.

Mineral	Occurrence (%)
Quartz	80
6% of quartz with Fe coating	
1% of quartz with Fe + Zn or Cu coating	
Barite	4
Pyrite	3
Plagioclase Feldspar	2
Chalcopyrite embedded in quartz	1
Jarosite	1
Chlinopyroxine	<1
Chlorite	<1
Epidote	<1
Tephra – Glacier Peak	<1
Mica	<1

Table 2. Metals concentrations (mean) in solid waste samples at Red Shirt Mill, Alder Mill and Alder Mine ($\mu g\ g^{-1}$).

Sample Location	n	Cu	Cd	As
Red Shirt Mill – Surface	1	269	8	NA
Red Shirt Mill – 1 m	5	1169	41	NA
Alder Mill – Surface	4	239	19	NA
Alder Mill – 2 m	4	1037	10	NA
Alder Mine – Ore	3	6,161	65	NA
Forest Soil Below Alder Mine	1	527	57	30
Alder Mine Camp Soil	1	19	4	6
Poorman Cr Soil – Reference	1	<1	<1	3
WA Soil 90th Percentile	--	36	1	7
Spokane 90th Percentile	--	22	1	9

The pH of the groundwater in the tailings impoundment was < 3. Since most minerals are salts of weak acids and strong bases they are stable under alkaline conditions but tend to dissolve under acid conditions. As a result of this characteristic, most rocks and minerals (with the exception of quartz and SiO_2) are alkaline and can neutralize natural or contaminant acidity. The rate of neutralization is relatively fast for carbonate rocks, and slow for most silicate rocks, except for clays. The neutralization process is called chemical weathering.

The formation of acid mine drainage and acid rock drainage is essentially an accelerated weathering process. When parent rock materials that are high in sulfides, metals and metaloids within the lithosphere are crushed, which increases its reactive surface area, then deposited in contact with the atmosphere, hydrosphere, and biosphere, soluble cations and anions form complexes that contaminate surface and groundwater supplies. Cu and Cd were found at extremely high levels in groundwater from wells in the tailings impoundment at the Alder Mill (Table 4). The domestic well adjacent to the tailings impoundment contained no Cu or Cd but did contain high levels of As. Sediments in the Methow River from Twisp south to below the Red Shirt Mill and at its confluence with Alder Creek contained Cu at concentrations that exceeded area background levels (Table 5).

Table 3. Metals concentrations in filtered groundwater from wells in tailings impoundment at the Alder Mill and filtered surface water from a stream between the Alder Mill and the Methow River (μg L^{-1}). Also included are data for White's domestic well for comparison

Sample Location	Cu	Cd	As
Well 1	38,000	600	2
Well 2	41,000	0	1
Well 3	35,000	0	0
Well 4	NA	NA	NA
White's Domestic Well	0	0	335
Reference Well	0	0	1

Table 4. Concentration of Cu in sediments in the Methow River below Twisp and at the confluence of Alder Creek relative to area background levels based on USGS data for region, DOE natural background levels for soil, and sediment from above Twisp.

Sample Location	Cu: Mean	Range	90th Percentile
USGS Methow Basin Sediment			34
WA Soil			36
Methow above Twisp	24	18 – 43	
Methow River at Twisp	144	137 - 148	
Methow River at Alder and Red Shirt Mills	189	70 – 695	
Alder Creek at Methow River	139	126 - 173	

The major component of sand and silt fractions of sediments in the Methow River at RM 40, based on frequency of occurrence, was plagioclase feldspars at 26% (Table 5). Minor components were quartz at 14%; chlorite at 12%; and hornblende, magnetite/hematite, muscovite, zircone, and chlinopyroxine at 5-6%. Trace elements include apatite, epidote, ilmenite. When the silt fraction was analyzed by XRD, quartz was identified as a major component and smectite as a minor component. Chlorite, calcite, siderite, muscovite, and vermiculite were identified as trace minerals (Table 6).

Analyses of the clay fraction by IR spectrophotometry indicated the presence of gibbsite, quartz, and muscovite. Microcline, montmorillonite, and halloysite may also be present (Table 7). Clay mineralogy by K, Mg, and glycol oriented XRD identified the presence of kaolinite, chlorite, fledspar, mica, alumite, muscovite, and siderite (Table 8).

Secondary mineral coatings were observed on most sand grains. Coatings were variable and ranged from doscontinuous to coatings that covered the entire surface of the primary mineral. Energy dispersive X-ray spectroscopy (EDS) results indicate that the chemical compositions of the coatings were generally dominated by Fe with lesser amounts of Mg, Br, Na, K, Ca, and Ti (Table 9). The trace metal content of sediments seived to 63µm revealed the presence of Cu, Zn, Pb, As, Cr, and Cd (in order of decreasing abundance, Table 10). These trace elements are presumably components of the secondary Fe (oxide or carbonate) coatings and not the result of primary mineral dissolution reactions.

Table 5. Sand and Silt Mineralogy by Microprobe Analysis

Mineral	Occurrence (%)
Plagioclase	26
K-Feldspar	6
Quartz	14
Chlorite	12
Hornblende	6
Magnetite/Hematite	6
Muscovite	6
Zircon	5
Chlinopyroxine	5
Apatite	3
Epidote	3
Ilmenite	3
Glass	2
Tephra (Altered Volcanic Fragment)	2
Oxides: Fe, Ti, Rare Earth (La Series)	

Table 6. Silt Mineralogy of Randomly Oriented Powder Mount by XRD

Mineral	Occurrence
Quartz	Major
Smectite	Minor
Chlorite	Trace
Calcite	Trace
Siderite	Trace
Muscovite	Trace
Vermiculite	Trace

Table 7. Clay Mineralogy by IR Spectrophotometry

Mineral	% Transmittance
Gibbsite and Microcline	9
Gibbsite and Quartz	49
Montmorillonite and Halloysite	10
Halloysite	16
Muscovite (536 cm^{-1})	27
Muscovite (3628 cm^{-1})	38

Table 8. Clay Mineralogy by K, Mg and Glycol Oriented XRD

Mineral	Occurrence
Kaolinite	Major
Chlorite	Major
Feldspar	Major
Mica	Minor
Alumite	Minor
Muscovite	Trace
Siderite	Trace

Table 9. Characterization of Oxide Coatings by SEM-EDS

Name	Elements/Mineral	Additional Elements/ Coating
Quartz	Si	Fe, Mg, Br, Na, K, Ca,Ti
Feldspar	Si, Al, Ca, Na	Fe, K
Ferricrete	Si, Al, Mg, K, Ca, Fe	Not Applicable
Ilminite	Ca, Si, Ti, Fe, Al	Fe, K

Table 10. Trace Metal Content of Sediments by ICP-AES

Element	Background	Concentration (ppm)
As	< 7	82
Cd	6	12
Cr	26	28
Cu	30	655
Pb	12	88
Zn	114	248

Plagioclase is Na-Ca Feldspar found primarily in granitic pegmatites. Quartz is a major constituent of igneous rocks such as granite. Quartz is also abundant in metamorphic rocks such as schists and gneisses derived from sedimentary rock. Hornblende and the mica muscovite comprise approximately 8% of granite whereas magnetite/hematite, zircon, and ilmanite are minor accessory minerals in granite (Mason 1968). Magnetite and hematite are low temperature hydrothermal vein minerals. K-feldspar is also found in granite and hydrothermal veins. Chlorite is of secondary origin and is common in metamorphosed siliceous rocks such as schists.

These observations are consistent with and reflect the geology and soil types described by Barksdale (1975) and the USDA Soil Conservation Service (1980) respectively. Mason (1968) described the origin of igneous and metamorphic rocks as occurring when magma solidifies within the earth’s crust. The major constituents of magma include O, Si, Al, Ca, Mg, Fe, Na, and K. Magma also contains minor elements in a residual liquid. The residual solutions give rise to pegmatites and hydrothermal veins commonly in fissures in the parent material. Veins consist of minerals deposited from hydrothermal solutions that have filled a fissure solidly from wall to wall.

Quartz and feldspar are the primary minerals in the sand and silt fractions of sediment from the Methow River reflecting area soils which are materials weathered from granite, gneiss, and schist. The granite indicates plutonic (intrusive) igneous origins. The dominant components of the clay fraction include gibbsite, quartz, and muscovite. Minerals such as sphalerite (ZnS), chalcopyrite ($CuFeS_2$), and galena (PbS) were not detected and the elements Zn, Cu, and Pb that were detected by ICP-AES must, therefore, be present as cations adsorbed to coatings on the surface of other primary minerals. Coatings on the surface of sediment particles and amorphic concretions containing smaller sediment particles, organic matter, and diatoms cemented together (ferricrete) appear to be forms of iron, e.g., siderite ($FeCO_3$) or goethite (FeOOH).

Transport

Potential sources of mine waste contamination affecting groundwater and river sediments include waste rock piles and mill tailings impoundments. Metals are released into the environment at various rates and concentrations because they are present in minerals and minerals are subject to dissolution caused by chemical weathering. Mining reduces ore to small particles with increased surface area and accelerated weathering rates. If oxidation of sulfide minerals also occurs then acid mine and acid rock drainage can enhance mobility of metals.

$$FeS_2(s) + {}^{15}/_{4}\, O_2 + {}^{7}/_{2} H_2O(l) \rightarrow \mathbf{FeIII(OH)_3(s)} + 2SO_4(aq) + 4H^{+}(aq)$$

Metals occur in a variety of chemical forms or species that can vary widely in solubility, mobility, toxicity, and bioavailability. In mine tailings or waste piles, metals can occur in primary minerals, secondary minerals formed by weathering of primary minerals *in situ*, solid precipitates formed by reactions of contaminant ions in groundwater with other aqueous ions, and adsorbed species. Although there are methods available to determine the types of solid phases present in a contaminated soil or mine tailings sample the concentration levels of heavy metals and metalloids they contain, it is more difficult to assess the importance of adsorbed metal or metalloid species at low surface coverages. Adsorbed species may comprise a significant fraction of the metal or metaloid present, and they are often the most bioavailable fraction. However, extraction methods (DPTA) that simulate bioavailability can be used to associate exposure to toxicity.

Low pH dissolves minerals including pyrite, which releases cations that are adsorbed onto the surfaces of mineralsurfaces in the vicinity of the dissolving pyrite. Acidic and reducing conditions causes desorption of cations from mineral surfaces and increases bioavailability.

Anaerobic conditions are also conducive to bacterial sulfate reduction (BSR), which leads to the precipitation of zinc, copper, and cadmium as insoluble sulfice minerals. Many treatment strategies, such as the use of constructed wetlands, rely on anaerobic conditions to precipitate heavy metals as insoluble sulfides. The acid mine and acid rock drainage associated with the Alder Mine and Alder Mill sites were high in sulfate (Table 11). Sulfate concentrations decreased but were significantly above reference sample background levels except at spring inputs to the Methow River. Although the strong odor (i.e., rotten eggs), which is characteristic of sulfide, was not apparent in any of the samples, FeS cubes and spheres containing Cu, Zn and As, with diameters in the range of 0.1 to 10 μm, were detected in the pore water from sample wells in the tailings impoundment at Alder Mill (Figure 9). Iron oxyhydroxides were also detected as precipitates where groundwater enters the Methow River.

Although there are methods available to determine the types of solid phases present in tailings or contaminated sediments, the concentration levels of heavy metals and metalloids they contain is more difficult to assess when the are present at low surface coverages or in trace concentrations. Adsorbed species may comprise a significant fraction of the metal or metaloid present, and they are often the most bioavailable fraction. However, extraction methods that simulate bioavailability can be used to associate exposure to toxicity.

Table 11. Sulfate concentration in acid mine drainage, tailings pore water, surface water, and groundwater samples.

Sample Location	n	Mean	Standard Deviation
Reference Sites			
Methow River Above Mine Inputs	18	2	1
Twisp River	4	3	1
Reference Wells	8	11	8
Contaminated Sites			
Alder Mine AMD	9	553	183
Alder Creek at AMD Outfall	10	31	12
Alder Creek at Methow River	4	57	14
Tailings Pore Water	8	785	257
Domestic Well Water – T. White	6	90	26
Methow River Input at Red Shirt Mill	6	4	2
Methow River Input at Alder Mill	7	8	4

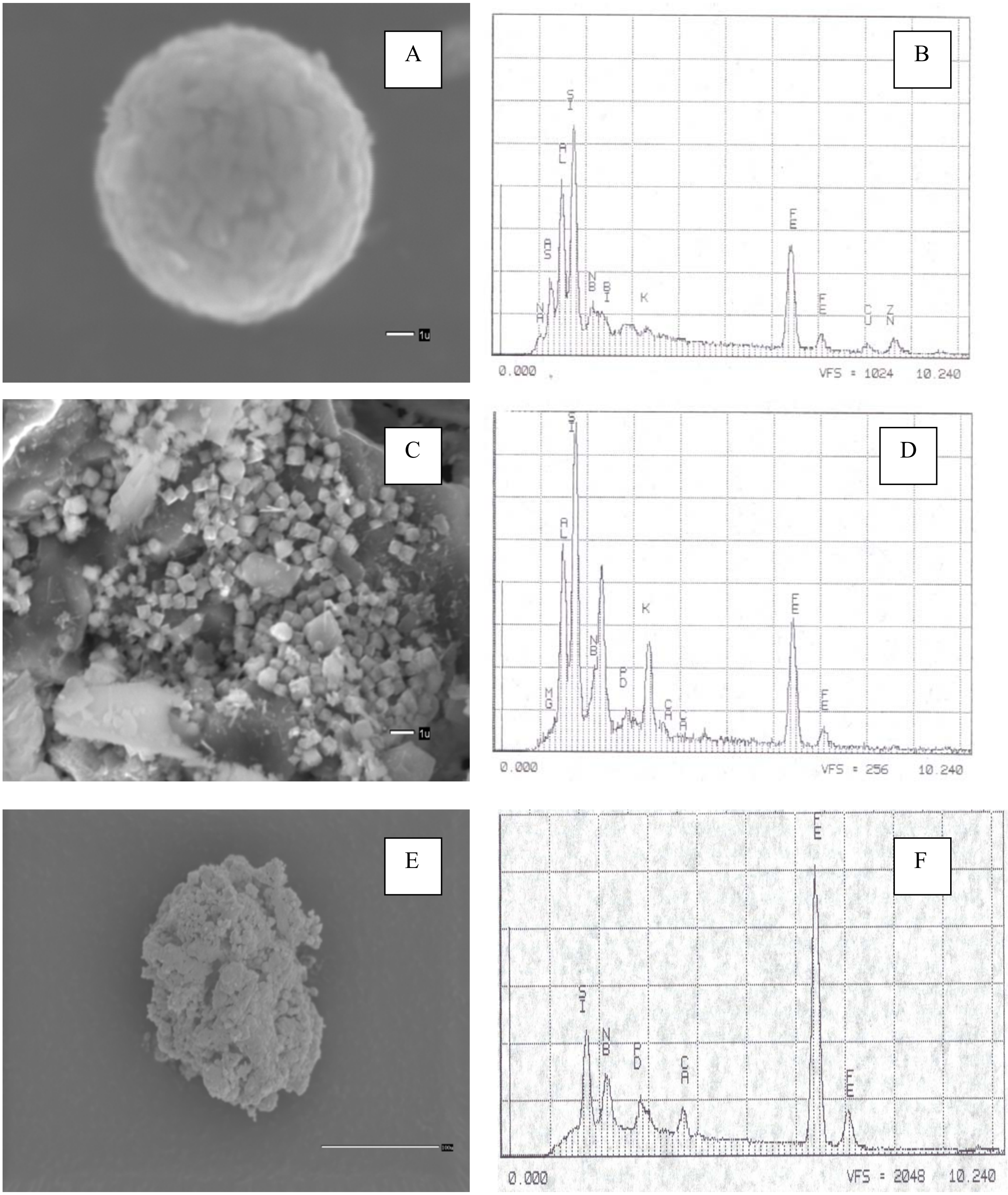

Figure 9. A) SEM photomicrograph, B) EDS spectrum, colloid sphere containing Zn, Cu and As from tailings pore water sediment particle; C) SEM photomicrograph, D) EDS spectrum, pyrite cubes from tailings pore water sediment partecle ; E) SEM photomicrograph, F) EDS spectrum, iron oxyhydroxide precipitate in groundwater input to Methow River.

Migration pathways of greatest interest here are surface water and groundwater. The migration pathway that is likely responsible for the contamination of groundwater supplies is infiltration from precipitation where fractures may be serving as pathways for groundwater contamination and inputs to the Methow River. Observations of bedrock morphology include extensive faulting and fractures and the presence of calcite fracture fillings, which suggest there is a potential that calcite fracture fillings are dissolving.

If calcite fracture fillings are being dissolved by waters infiltrating from the surface then the processes of $CaCO_3$ dissolution can result in modifications to the hydrologic character of the bedrock. Once calcite-cemented fractures open the porosity, the reactive character of the rock can be increased. Evidence to support this hypothesis is provided by the Cl-tracer injection study performed at Alder Mine. At a distance of 322 m between the adit and the input to Alder Creek, peak Cl and electrical conductivity was detected at the input to Alder Creek 3-hours following tracer injection at the mine adit. Rate of flow, therefore, was equal to approximately (107 m hr^{-1}). Unrestricted flows through open fractures is, therefore, indicated.

The process of colloid facilitated transport, described by Kretzschmar et.al. (1999), is the likely mechanism for the translocation of adsorbed metal contaminants from the abandoned mine sites to the Methow River. Solids with a diameter between 0.01 and 10 μm are considered colloids (Stumm and Morgan 1996). Coarser particles are considered suspended particles. To be dissolved, therefore, a molecule must have a diameter of < 0.01 μm. If present, some colloidal solids will pass through a 0.45 μm filter membrane used to distinguish dissolved from suspended metals. According to the colloid facilitated transport model, metals partition between the surfaces of immobile matrix particles, the aqueous phase, and mobile colloidal particles, which are transported with flowing water. While strongly sorbing contaminants can be highly retarded by immobile matrix particles, colloidal carriers can provide a rapid transport mechanism.

Sampling and characterization of mobile colloids is difficult and there are few studies that focus on the subject (Kretzschmar et. al. 1999). Generally, zero tension lysimeters are used to sample for mobile colloids, but artifacts are a problem since disturbances cannot be avoided during installation. There are numerous techniques available to characterize colloids. ICP-AES can be used to analyze bulk samples and Energy dispersive X-ray analysis can be used to determine the composition of single particles viewed under a scanning electron microscope. Detection limits, however, are high (500-1000 mg g^{-1}). Greater sensitivity can be achieved using synchrotron-based microbeam methods such as synchrotron X-ray fluorescence spectroscopy. Details regarding the mobility of subsurface colloids are outside the scope of this project and no further work will be done to characterize this transport mechanism.

6. BIOLOGICAL EFFECTS OF INORGANIC CONTAMINANTS IN THE METHOW RIVER

6.1 Introduction

The objective of this study was to determine the sediment and food chain transfer of inorganic contaminants (As and Cu) from abandoned mine sites near Twisp, WA to organisms in the Methow River. Goal. Specific goals are to measure sediment and metal content of periphyton in Methow River between Twisp and sites below Red Shirt Mill relative to unimpacted sites above Twisp, determine whether invertebrates in contaminated sediments in the Methow River concentrate metals, and determine pathological impacts that result from exposure of juvenile trout in a Methow River side channel to ambient levels of metals from an abandoned mine.

6.2 Materials and Methods

Periphyton samples were collected from rocks at sites colonized by the caddis fly *Ecclisomyia.* Metal content of periphyton from pool at confluence of Twisp River and Methow River, between Alder Mill and Red Shirt Mill, and from pool below Red Shirt Mill collected in August were measured. Periphyton was not collected for analysis from site 1 km above Twisp where sediment metal concentrations were equivalent to background metal concentrations. Further analyses will be conducted on periphyton from all sites during the 5th and 6th quarters.

Invertebrates from sites where sediment samples were collected in the Methow River were analyzed for metal accumulation. Whole body metal content of 5th instar larvae from a pool at confluence of Twisp River and Methow River, between Alder Mill and Red Shirt Mill, and from pool below Red Shirt Mill collected in August were measured. No larvae were available for analysis from site 1 km above Twisp where sediment metal concentrations were equivalent to background metal concentrations. *Ecclisomyia* larvae exposed in-vitro to a 50/50 mixture of fixative and acid mine drainage (AMD) were dissected and analyzed.

Thin sections of midgut epithelial cells from *Ecclisomyia* were examined by TEM and compared to cells from larvae not exposed to AMD. Granules of divalent cations were observed in the mitochondria of exposed cells. The effects of metals on the mitochondria of impacted cells from exposed animals will be evaluated for use as an indicator of heavy metal exposure and toxicity in invertebrates and in trout.

A biological assessment was submitted to National Marine Fisheries Service and Fish Transport Permit Application was submitted to Washington Department of Fish and Wildlife in first quarter FY00. Letters of concurrence were received from NMFS and USFWS in second quarter FY00. Met with WDFW to inspect pens and study sites. Received fish transport permit in February, 2001.

Trout exposure and toxicity study is scheduled to occur during the second year. Thin sections of epithelial cells from gill, liver, kidney and gut epithelia will be examined by TEM and compared to cells from trout not exposed to metals in contaminated water. The effects of metals on the mitochondria of impacted cells will be used as an indicator of heavy metal exposure and toxicity.

6.3 Results and discussion

Source

Infiltrating water dissolves primary (hypogene) minerals at near-surface conditions producing a leached zone, and deposits the soluble species of secondary (supergene) minerals downstream producing secondary enrichment zones (Figure 10) by a process called supergene enrichment.

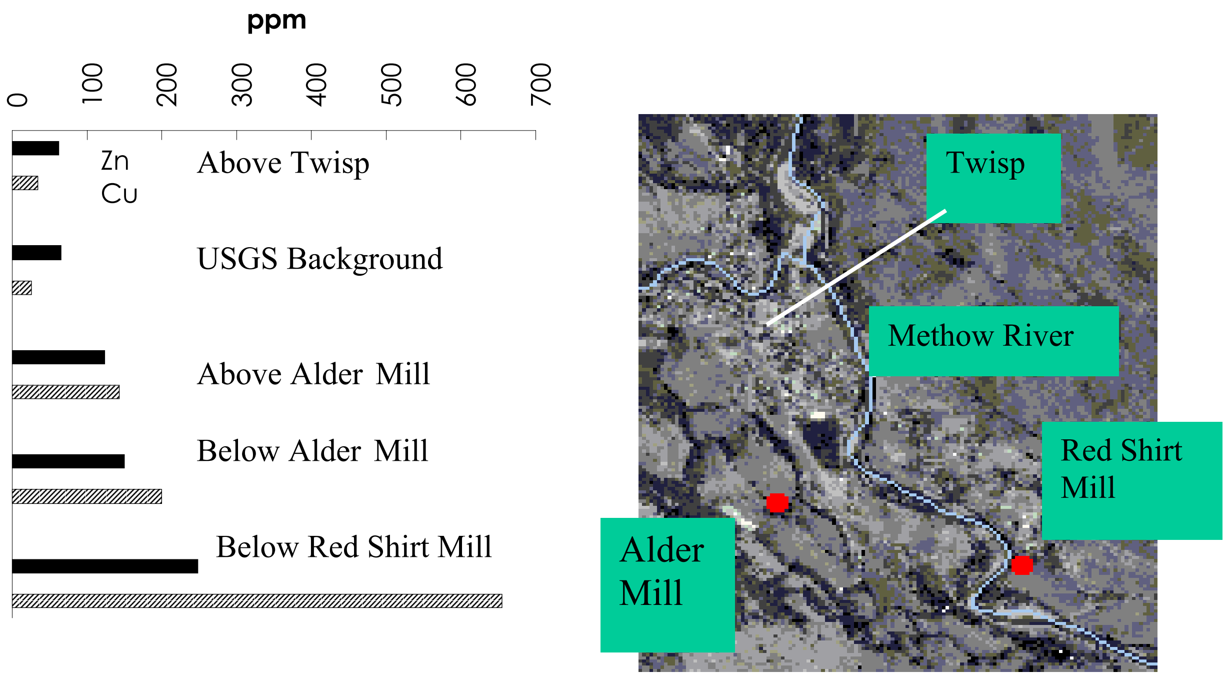

Figure 10. Abandoned mill sites and sediment metal concentrations in Methow River near Twisp, Okanogan County, Washington. Heavy metals are generated in an area where faults and other geologic features provide pathways for contaminating surface and groundwaters to travel downgradient from the site.

Sediments

Quartz and feldspar are the primary minerals in the sand and silt fractions of sediment from the Methow River. Minerals such as sphalerite (ZnS), chalcopyrite ($CuFeS_2$), and galena (PbS) were not detected and the elements Zn, Cu, and Pb that were detected by ICP-AES must, therefore, be present as cations adsorbed to coatings on the surface of other primary minerals (Figure 11). Coatings on the surface of sediment particles and amorphic concretions containing smaller sediment particles, organic matter, and diatoms cemented together (ferricrete) appear to be forms of iron, e.g., siderite ($FeCO_3$) or goethite ($FeOOH$).

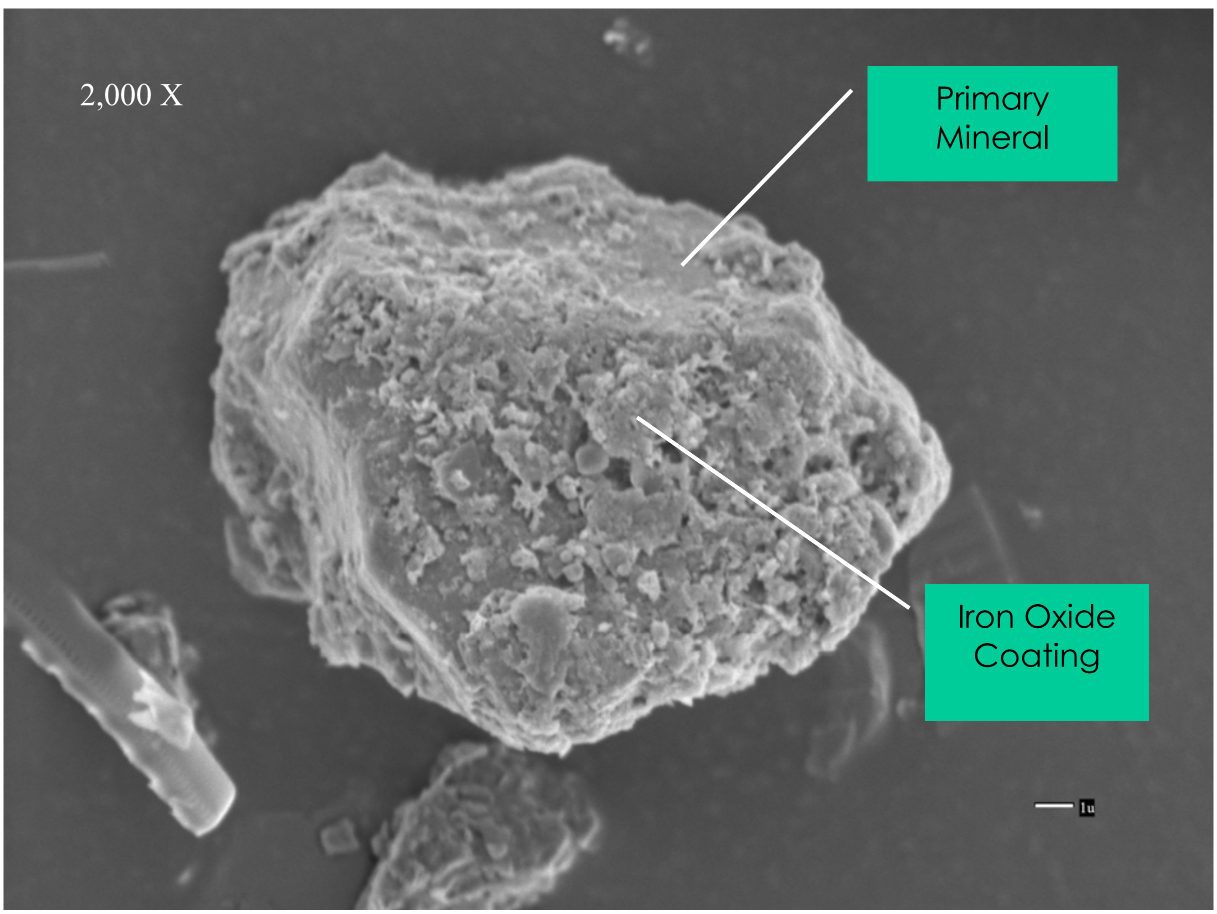

Figure 11. Iron oxide coating on surface of feldspar particle that adsorbs and transports heavy metal ions from source to biological endpoint as a suspended solid. (Scanning Electron Micrograph).

Aquatic Insects

Benthic macroinvertebrates provide an excellent model system to directly examine the effects of metal contaminants on the environment (Figure 12). Because aquatic insects reside in freshwater and contain more salts (hypertonic) than the medium in which they live, water has a tendancy to enter and salt diffuse out. Insect cells have, on the inside surface of their ailimentary canal, mechanisms that actively excrete water and take up salts. Ion regulation occurs in the midgut region of the ailimentary canal.

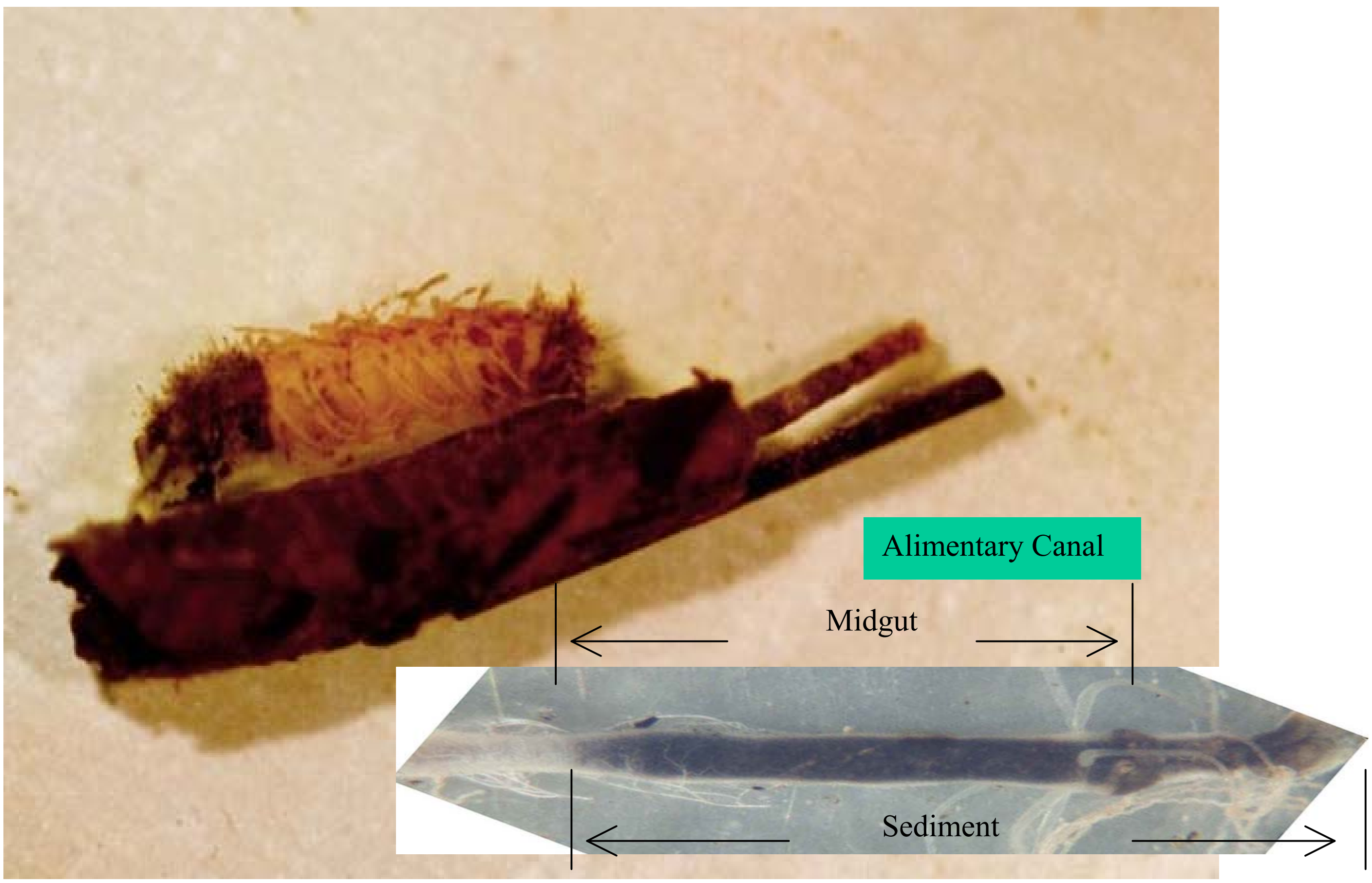

Figure 12. The tube-case making caddisfly larvae *Ecclisomyia* from the Methow River. Inset shows its ailimentary canal removed containing accumulated sediments ingested with food.

Histopathology

In cells that actively transport ions (salts), numerous mitochondria are located near the cell surface so that the energy source is located close to where the active transport mechanisms reside (Figure 13). Electron microscopic evidence presented by Peachy (1964) showed that the divalent cations calcium, strontium, and barium accumulated in granules in the mitochondria of whole cells of toad urinary bladder and isolated rat kidney mitochondria. These granules help regulate the internal ionic (salt) concentration in the mitochondria.

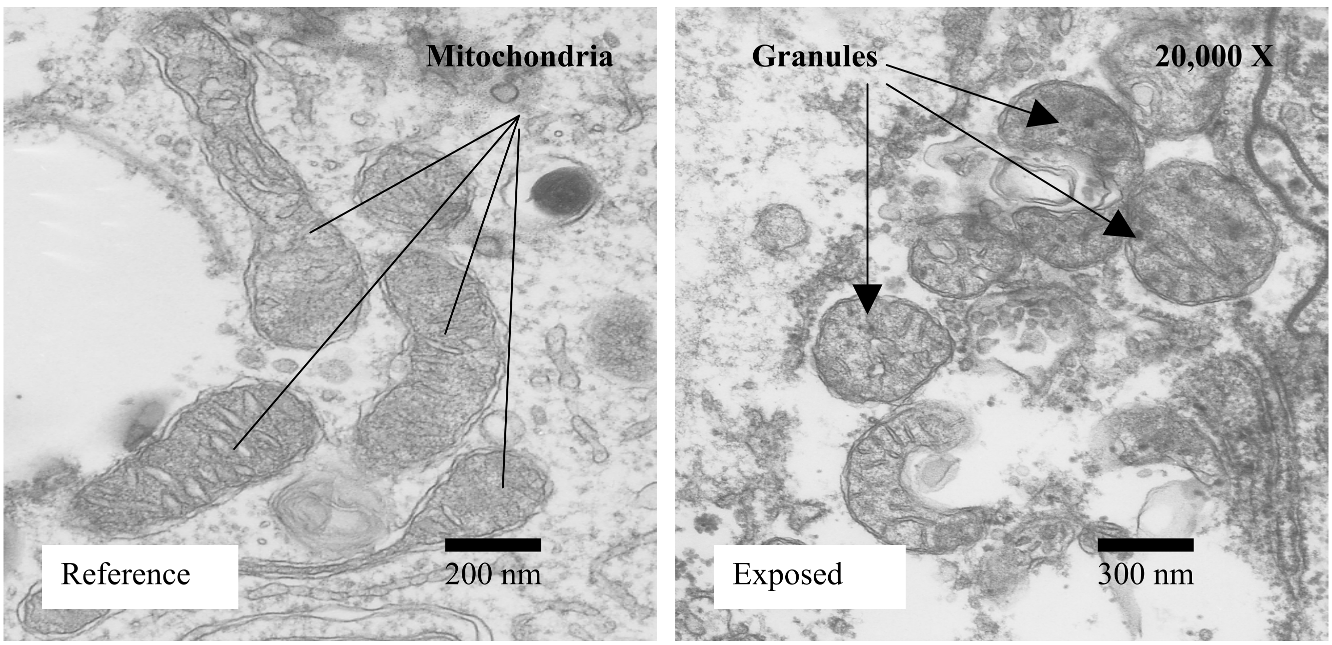

Figure 13. Granules in the gut-cell mitochondria of the caddis fly *Ecclisomyia sp.* from the Methow River after exposure to mine waste containing the heavy metals Cd, Cu, Cr, Se and Zn. These granules indicate heavy metals are present in unusual concentrations in the fluid bathing intact cells and the mitochondria they contain. (Transmission electron micrograph).

Conclusions

Sediments cause adverse effects on aquatic biota even where waters meet water-quality guidelines. The elements Zn, Cu, and Pb that were detected by ICP-AES appear to be present as cations adsorbed to coatings on the surface of other primary minerals. The accumulation of particulate metals and the formation of granules containing divalent cations by the caddis fly *Ecclisomyia sp* demonstrates the importance of dietary exposure to metal uptake. Although metals are regulated in the environment based on the dissolved fraction, this study shows that food is important in the transfer of metals in aquatic food webs, which poses a risk of toxicity in endangered salmonids in the Methow River.

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